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PATENT SPECIFICATION

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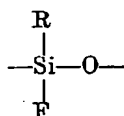
COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of New Organofluoro-Siloxane Products

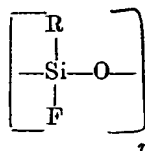
We, THE DOW CHEMICAL COMPANY, a corporation organized under the laws of the State of Michigan, United States of America, whose address is Midland, Michigan, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention concerns certain new organofluorosiloxane products and their preparation.

The products of this invention are organofluorosiloxane condensation products which contain in the molecule structural units of the formula:



in which R represents a hydrocarbon radical selected from the group consisting of alkyl, aryl and aralkyl radicals. The invention is particularly concerned with such organosiloxanes which contain a radical:



where R has the meaning just given and n is a whole number greater than 1.

The organofluorosiloxanes having the above general formulas contain silicon atoms having hydrocarbon radicals and fluorine atoms attached directly thereto. These polymeric products may be composed of linear molecules comprising two

or more silicon atoms connected to each other by oxygen atoms and terminated by end-blocking groups such as a hydroxyl group, (—OH), an alkoxyl group, (—OR), a trialkylsiloxy group, (—OSiR₃), etc.; or cyclic molecules containing three or more silicon atoms. Frequently, mixtures of both types are obtained.

The products vary from thin liquids to hard solids. The physical properties of the organofluorosiloxane polymers are dependent to a large extent upon the nature of the hydrocarbon radical attached to the silicon atom. When the organic portions of the molecule consist of hydrocarbon chains, each containing 12 or more carbon atoms, the polymers are frequently waxy or rigid solids.

The present invention is derived from applicant's discovery that when an organo-polyhalosilane wherein at least one of the halogen atoms is fluorine, is subjected to hydrolysis, all of the halogen is very readily removable by hydrolysis except for a single fluorine atom, but that fluorine atom which remains is very difficult to remove by hydrolysis and can be removed only under unusually vigorous hydrolysis conditions. Such is not the case in the hydrolysis of methylsilicon chlorides, bromides, or iodides, as methyl-trichlorosilane, for example, readily undergoes hydrolysis to remove all of the chlorine atoms of the organohalosilane starting material.

Accordingly the present invention consists in the preparation of organofluorosiloxanes by hydrolyzing under moderate hydrolysis conditions organofluorosilanes having the general formula RFSiX₂, where R represents a hydrocarbon radical and X is a readily hydrolyzable group, such as a halogen atom, a hydrocarbonoxy radical, an amino group etc. Examples of satisfactory hydrolyzable organofluorosilane starting materials include alkyl,

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aryl and aralkyl trifluorosilanes, alkyl, aryl and aralkyl difluoro chlorosilanes, alkyl, aryl and aralkyl difluoro bromosilanes, alkyl, aryl and aralkyl dichloro fluorosilanes, alkyl, aryl and aralkyl dibromo fluorosilanes, alkyl, aryl and aralkyl difluoro alkoxy silanes, alkyl, aryl, and aralkyl dialkoxy fluorosilanes, etc.; or mixtures of such organofluorosilanes with other readily hydrolyzable organosilanes, e.g. dialkyl dibromosilanes, aryl trichlorosilanes, etc. When an organofluorosilane and a non-fluorinated hydrolyzable organosilane are co-hydrolyzed and condensed, copolymers are obtained which contain in the molecule structural units of the formula: $-R_2FSiO-$.

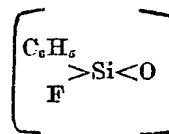
The hydrolysis may be conducted at ordinary or elevated temperatures by the addition of water to the organofluorosilane starting material. It is usually advantageous to carry out the reaction in the presence of an inert solvent, e.g. an ether, an aliphatic or aromatic hydrocarbon, a halo-hydrocarbon, etc., at the boiling point of the mixture. The solvent is one which is effective in dissolving the organofluorosilane starting material. It usually also dissolves the organofluorosiloxane product, but this is not essential. Condensation of the hydrolysis products occurs simultaneously with the hydrolysis reaction and results in the production of organosiloxane polymers containing silicon atoms joined to other silicon atoms through silicon-oxygen-silicon linkages and having hydrocarbon radicals and fluorine atoms attached directly to said silicon atoms. A condensation catalyst such as a mineral acid may be added prior to the reaction, but is not required. The reaction products are subsequently separated, washed free of acid and purified, e.g. by distillation therefrom of solvent or other impurities. The resultant product comprises volatile organofluorosiloxanes of relatively low molecular weight, that is, polymers having an average of 10 or less silicon atoms in the molecule, and frequently containing residual groups, such as hydroxyl groups, capable of further condensation. Mild oxidation or heating at temperatures in the order of 50°—200° C. or thereabouts results in increase in polymer size and eventual formation of hard, insoluble resinous materials. It is characteristic of the liquid polymers that they may be converted to tack-free solid bodies by exposure of a thin film thereof to air at ordinary temperatures. Accordingly, the organofluorosiloxanes are valuable as resinous coatings for metals, ceramics, textiles, paper, etc.

The fluorine atom which is attached to the silicon atom in these organofluorosiloxanes is not affected by ordinary methods of hydrolysis, but under very vigorous reaction conditions, e.g. in the presence of alkalis, may be replaced by oxygen to create further siloxane linkages. The fluorine may also be reacted with metal alcoholates or metal salts of carboxylic acids to cause displacement by an organic radical. Accordingly, the organofluorosiloxanes may be employed for the preparation of a wide variety of organosilicon compounds. They are also useful as fungicides, hydrophobing agents, and protective coatings.

The following examples illustrate specific modes of applying the principle of the invention, but are not to be construed as limiting its scope:

EXAMPLE 1.

A mixture of 30.1 grams (0.186 mol.) of phenyl trifluorosilane in 87.9 grams of benzene was added slowly and with stirring to 100 grams of water while maintaining the mixture at a temperature of approximately 25° C. When the addition was complete, the temperature was raised to approximately 70° C. for 4 hours. The oily product which was obtained was washed with water and concentrated by heating to 160° C. at 25 millimeters absolute pressure. A slightly cloudy oil remained which had a viscosity of 100 centistokes. Analysis showed a fluorine content of 14.0 per cent., and a silicon content of 19.8 per cent., indicating an average composition of



A portion of the oil was placed on a watch glass and heated in an oven at 150° C. After 3 hours of heating, the oil had become viscous; after 20 hours the product was a soft, gummy, slightly tacky coating which adhered tenaciously to the glass surface. The film was insoluble in hot benzene.

In another experiment, a portion of the oil on a watch glass was heated at 250° C. At the end of 1 hour, the oil had become viscous; at the end of 4 hours, a clear tough, tack-free gum was obtained, which was quite resistant to abrasion and adhered tenaciously to the glass.

EXAMPLE 2.

A solution of 34.0 grams of octadecyl trifluorosilane in 60 grams of toluene was added slowly and with stirring to approximately 100 grams of water. The reaction mixture was allowed to stand with stirring at 85°—90° C. for about 14 hours, at which time another 100 gram portion of water was added, and stirring continued for another 5 hours. The oily product was washed several times with water and was then heated stepwise to 126° C. at 20 millimeters absolute pressure, to volatilize solvent, and water.

The residue consisted of approximately 32.5 grams of a hard, brittle wax-like polymer, which contained 4.5 per cent. of fluorine. A 50 per cent. toluene solution of the material had a viscosity of 4.7 centistokes. The solution was spread on a glass microscope slide. The film air-dried at room temperature in 0.5 hour to a smooth hard coating.

EXAMPLE 3.

A solution of 16.9 grams of phenyl diethoxy fluorosilane (C_6H_5) (C_2H_5O)₂SiF, in 66 grams of benzene was added slowly and with stirring to a mixture of approximately 75 grams of water and 20 grams of normal hydrochloric acid. The mixture was allowed to stand with stirring for 4 hours. During these operations, the mixture was maintained at approximately 23°—25° C.

The oily layer which separated was removed, washed repeatedly with water, and concentrated by heating to 100° C. at 40 millimeters absolute pressure. The residue comprised a slightly cloudy oil which had a viscosity of 458 centistokes at 25° C. Analysis showed a fluorine content of 12.7 per cent.

A benzene solution containing from 30 to 50 per cent. by weight of the oil was applied as a coating to unglazed paper sheets, and allowed to air-dry overnight. There was produced a tack-free, smooth, flexible transparent paper.

A portion of the oil on a watch glass was heated in an oven at 250° C. After 1 hour of heating, the oil had become quite viscous. During 20 hours of heating, it was converted to a clear, tough, tack-free gum which adhered tenaciously to the glass, and was quite resistant to abrasion.

EXAMPLE 4.

A solution of 23 grams of ethyl dichlorofluorosilane, $C_2H_5SiCl_2F$, in 87.9 grams of benzene was added slowly and with stirring to 100 grams of water, while maintaining the mixture at a temperature of approximately 20° C. When the addition was complete, the mixture was allowed to stand, with stirring, for 30 minutes.

The resultant oil was separated, washed twice with water, and subsequently was heated to approximately 90° C. at 30 millimeters absolute pressure to volatilize residual water and solvent. The oily product was slightly cloudy, and had a viscosity of 9.5 centistokes.

A portion of the oil on a watch glass was heated for 1 hour at 150° C. The oil became very viscous. Heating was continued for 20 hours, at which time the sample had become a tack-free, rubbery gel.

EXAMPLE 5.

A mixture of 1 gram of phenyl dichlorofluorosilane and 19.3 grams of phenyl ethyl dichlorosilane was slowly added to and hydrolyzed by reaction with 57 grams of tertiary butyl alcohol at from 50°—60° C., with stirring. The reaction mixture was then heated at 90° C. at 7 millimeters absolute pressure to volatilize low boiling components, e.g. tertiary butyl chloride. The residual product, consisting of 15.5 grams of a clear, light amber colored oil, had a viscosity of 97.8 centistokes. Analysis showed a fluorine content of 1.40 per cent., and a chlorine content of 0.63 per cent.

Heating a portion of the oil at 250° C. for 3 hours resulted in a loss in weight of 52 per cent. The residual oil was very viscous.

EXAMPLE 6.

By procedure similar to that described in Example 5, tolyl dichlorofluorosilane, $CH_3C_6H_4SiCl_2F$, (0.179 gram mol.), was reacted with tertiary butyl alcohol, (0.47 gram mol.), in the presence of benzene as a reaction medium at a temperature of from 30°—40° C. After removal of solvent and volatile reaction products, there remained a cloudy, colorless oil which had a viscosity of 1458 centistokes.

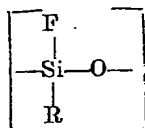
By procedure similar to that described in preceding examples, benzyl trifluorosilane may be reacted with water to produce benzyl fluorosiloxane polymers; phenethyl dichlorofluorosilane may be employed as the starting material to produce phenethyl fluorosiloxane polymers; dodecyl dibromofluorosilane may be employed to produce dodecyl fluorosiloxane polymers.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of making an organo-fluorosiloxane condensation product, containing silicon atoms having hydrocarbon radicals and fluorine attached thereto, which method comprises hydrolyzing under moderate hydrolysis conditions an

organofluorosilane having the general formula RFSiX_2 , wherein R represents a hydrocarbon radical and X represents a readily hydrolyzable group.

- 5 2. A method according to claim 1 of making an organofluorosiloxane condensation product which contains in the molecule a structural unit:—



n

- 10 wherein n is a whole number greater than 1, in which the organofluorosilane having the general formula RFSiX_2 , wherein X represents chlorine or bromine is hydrolyzed under moderate hydrolysis conditions by reacting it with water.

- 15 3. A method, as claimed in either of the preceding claims, wherein the hydrolysis is carried out in the presence of an inert solvent for the organofluorosilane.

- 20 4. A method, as claimed in any of the preceding claims, wherein the hydrolysis is accomplished by heating the reaction mixture to boiling at atmospheric pressure.

5. A method, as claimed in any of the 25 preceding claims, wherein the organofluorosiloxane condensation product resulting from the hydrolysis reaction is subsequently subjected to a mild oxidation.

6. A method, as claimed in any of 30 claims 1 to 4 wherein the organofluorosiloxane condensation product resulting from the hydrolysis reaction is subsequently exposed to air.

7. A method of making an organofluorosiloxane condensation product, 35 which contains silicon atoms having fluorine and a hydrocarbon radical attached thereto, substantially as described in any of examples 1—6 herein.

8. An organofluorosiloxane condensation product, containing silicon atoms 40 having fluorine and a hydrocarbon radical attached thereto, when prepared by the method of any of the preceding claims.

Dated the 20th day of June, 1947.

ELKINGTON & FIFE,
Consulting Chemists, and
Chartered Patent Agents,
Bank Chambers, 329, High Holborn,
London, W.C.1,
Agents for the Applicants.

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